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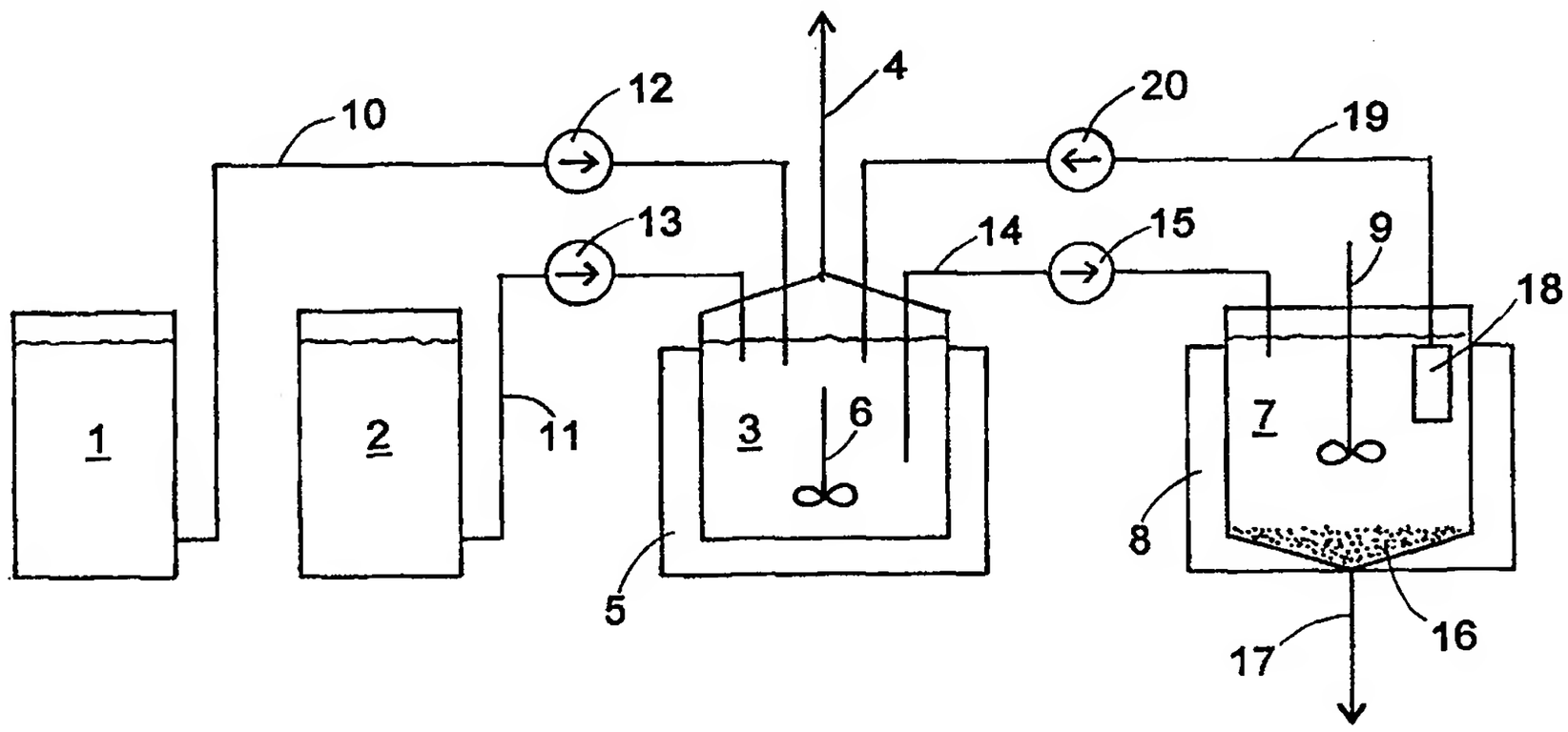
(54) **Title:** METHOD OF PRODUCING DINITRAMIDE SALTS



(57) **Abstract**

The invention relates to a method of producing organic dinitramide salts, for instance, guanidine dinitramide and guanylurea dinitramide starting from ammonium dinitramide (ADN). A concentrated aqueous solution of ADN is reacted with a concentrated aqueous solution of an organic salt, whose anion is OH^- or CO_3^{2-} which is capable of taking up a proton from the ammonium ion of ADN and transferring said ion to ammonia. The formed by–products, i.e. ammonia and possibly carbonic acid, are driven off from the solution, as well as a certain amount of water to maintain a concentrated solution. The organic dinitramide salt is then precipitated, for instance by cooling the solution. The method can be carried out as a continuous or semicontinuous process in a reactor (3), to which concentrated aqueous solutions of ADN (1) and organic salt (2), respectively, are supplied in equimolecular amounts. The solution is transferred from the reactor to a precipitation tank (7) where organic dinitramide salt (16) is precipitated and a supernatant is recirculated to the reactor.

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Method of Producing Dinitramide Salts

The invention relates to a method of producing organic dinitramide salts.

The production of dinitramide salts is described in, for instance, WO 97/06099. In this known method, dinitramide acid is prepared by nitration of various initial substances, whereupon the reaction mixture is neutralised with suitable compounds in order to obtain the desired dinitramide salt. Nitration is a relatively complex reaction and production of the dinitramide salt in pure form may require a great deal of processing equipment, which makes this method suited in the first place for large scale production.

Ammonium dinitramide (ADN) is the dinitramide salt which has attracted the greatest interest owing to its potential as a chlorine-free oxidiser in propellant compositions and which can be expected to be produced industrially in large quantities.

Other dinitramide salts having an organic cation can, however, have properties which make them especially suitable as an explosive or a component in specific explosive compositions.

For the production of such organic dinitramide salts, it may be more convenient to start from an existing dinitramide salt than to produce the desired salt directly via nitration.

Prior-art methods for converting a dinitramide salt into another dinitramide salt are usually based on an ion-exchange reaction, starting from, for instance, the silver or barium salt of the dinitramide ion and adding a suitable salt whose anion results in a precipitation with the silver or barium ion and the desired new salt remains dissolved. Two precipitation steps are thus required to obtain the desired product. There is always a risk of coprecipitation of the other product in the different precipitations in such a method, which results in a loss of yield and a purification problem.

According to the present invention, ADN is used as starting material (dinitramide ion source) to produce dinitramide salts having an organic cation. A quick and easy method obviating the above-mentioned purification problem is provided. The method is designed to give only by-products which can be driven off in gaseous

form from the reaction mixture, which permits the desired product to be precipitated from the remaining solution with great purity. The method can be carried out in an essentially closed water system and is suitable for continuous or semicontinuous production.

The invention is defined by the claims.

According to the invention, the organic dinitramide salt is produced by reacting a concentrated aqueous solution of ADN with a concentrated aqueous solution of an organic salt, whose anion is OH^- or CO_3^{2-} which is capable of taking up a proton from the ammonium ion of ADN and transferring said ion to ammonia;
driving off ammonia and, where appropriate, carbon dioxide from the aqueous solution, and concentrating, if required, the solution by driving off a certain amount of water, and
precipitating the organic dinitramide salt from the aqueous solution.

In the reaction, ammonia and water and carbonic acid, respectively, form, which can easily be driven off from the solution. What remains is merely a solution of the organic dinitramide salt, which spontaneously precipitates as the limit of saturation is exceeded.

The driving-off of the by-products can take place by heating the solution, possibly under reduced pressure if the desired organic dinitramide salt is heat-sensitive.

In addition to the removal of ammonia and, where appropriate, carbon dioxide, a certain amount of water is distilled off when necessary to give the solution a desired degree of saturation in respect of the organic dinitramide salt. Subsequently the solution can be cooled to precipitate dinitramide salt.

The method is intended above all for the production of dinitramide salts having an organic nitrogen-containing cation. These salts frequently have properties which in various contexts make them suitable as an explosive and as a component in propellants, explosives and pyrotechnical compositions. In the method, it is particularly preferred to use the carbonates of these nitrogen-containing compounds. Some of them can also be too sensitive to alkali to permit the production of hydroxides. Guanylurea dinitramide, which is disclosed in Swedish Patent Application 9701897-2, and guanidine dinitramide can advantageously be produced according to the

method, guanylurea carbonate and guanidine carbonate, respectively, being preferred as starting material.

The method can be carried out as a continuous or semicontinuous process, using an integrated and essentially closed water system, which will be described below with reference to the accompanying Figure.

Fig. 1 is a schematic view of an example of a process set-up for continuous or semicontinuous production of organic dinitramide salts according to the invention.

Fig. 1 illustrates a first storage tank 1 for a concentrated aqueous solution of ADN; a second storage tank 2 for a concentrated aqueous solution of an organic salt in the form of its hydroxide or carbonate; a reactor 3, which is provided with a waste gas duct 4, a heating device 5 and an agitator 6; and a precipitation tank 7, which is provided with a cooling device 8 and an agitator 9.

Through conduits 10, 11 and dosing pumps 12, 13, equimolecular amounts of ADN solution and organic salt solution, respectively, are pumped continuously or intermittently to the reactor 3, where the solutions are mixed. The basic anion (OH^- or CO_3^{2-}) of the organic salt reacts with the ammonium ion of ADN, and ammonia and water or carbonic acid form. The reaction mixture is heated in the reactor by means of the heating device 5, ammonia and, where appropriate, carbon dioxide (from the carbonic acid) being removed through the waste gas duct 4. A certain amount of water is normally also driven off so that the solution remains concentrated in respect of the organic dinitramide salt. A certain amount of the concentrated solution in the reactor 3 is pumped continuously or intermittently through the conduit 14 and the pump 15 to the precipitation tank 7, where the solution is cooled by means of the cooling device 8. Organic dinitramide salt 16 then precipitates when the limit of saturation is exceeded and can be discharged through an outlet 17. A certain amount of the concentrated supernatant in the precipitation tank is pumped continuously or intermittently through a filter 18, the conduit 19 and the pump 20 back to the reactor 3.

The invention will now be illustrated by way of examples.

Example 1

Solution 1: 2.0 g ADN was dissolved in 0.7 ml water.
Solution 2: 1.45 g guanidine carbonate was dissolved in 4.5 ml water.
The solutions were mixed, and a precipitate immediately formed. A smell of ammonia could be established. The precipitate was filtered off, washed 3 times with ice water and dried in a hot cabinet. The precipitate was identified by spectroscopic methods as guanidine dinitramide.

Example 2:

Solution 1: 10.0 g ADN was dissolved in 6 ml water.
Solution 2: 7.5 g guanidine carbonate was dissolved in 20 ml water.

Solution 2 was heated and solution 1 was added during agitation. Formation of carbon dioxide and ammonia could be established. When cooling the solution, a white precipitate of guanidine dinitramide immediately formed. The precipitate had high purity.

Claims:

1. A method of producing organic dinitramide salts, characterised by the steps of reacting a concentrated aqueous solution of ADN with a concentrated aqueous solution of an organic salt, whose anion is OH^- or CO_3^{2-} which is capable of taking up a proton from the ammonium ion of ADN and transferring said ion to ammonia; driving off ammonia and, where appropriate, carbon dioxide from the aqueous solution, and concentrating, if required, the solution by driving off a certain amount of water, and
precipitating the organic dinitramide salt from the aqueous solution.

2. A method as claimed in claim 1, characterised in that the anion of the organic salt is carbonate.

3. A method as claimed in claim 1, characterised in that the cation of the organic salt is a nitrogen-containing cation.

4. A method as claimed in claim 3, characterised in that the nitrogen-containing cation is selected from the group consisting of guanidine ion and guanylurea ion.

5. A method as claimed in claim 1, characterised by the steps of mixing the concentrated aqueous solutions of ADN and organic salt, respectively, in a reactor (3); heating the reaction mixture to drive off ammonia, optionally carbon dioxide and a certain amount of water; filling the reactor continuously or intermittently with concentrated aqueous solutions of ADN and organic salt, respectively, in equimolecular amounts, and transferring the solution continuously or intermittently from the reactor (3) to a precipitation step (7); cooling the solution in the precipitation step to obtain a precipitate (16) of the organic dinitramide salt and a supernatant concentrated in respect of organic dinitramide salt, and recirculating the supernatant continuously or intermittently to the reactor (3).

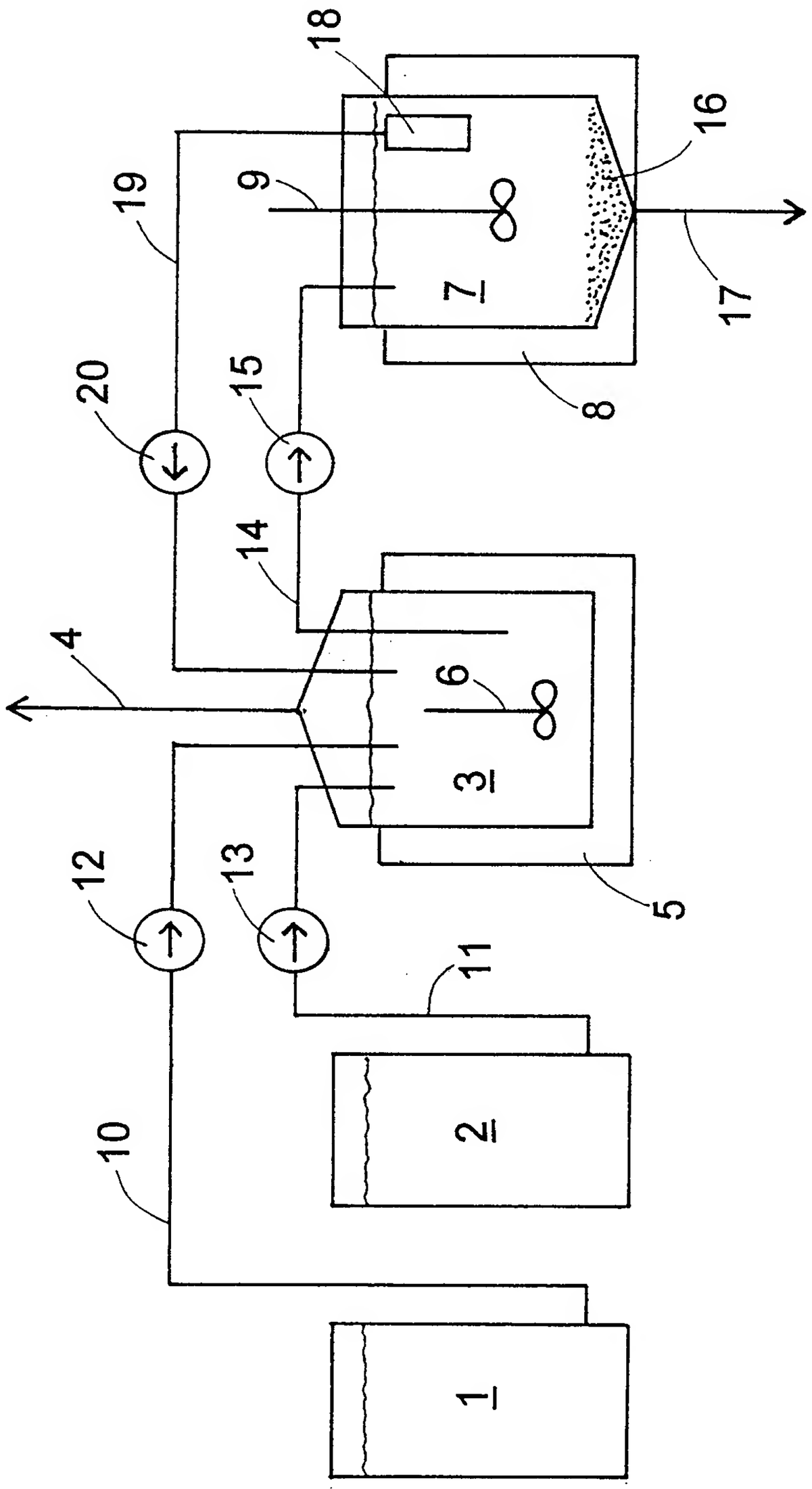

Fig 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 99/00308

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C01B 21/082, C06B 25/34
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01B, C06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

QUESTEL: WPIL; STN: REG. CA; DIALOG: DIALINDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9706099 A1 (FÖRSVARETS FORSKNINGSANSTALT), 20 February 1997 (20.02.97), page 2, line 10 - page 3, line 31 --	1-5
A	US 5415852 A (ROBERT J.SCHMITT ET AL), 16 May 1995 (16.05.95), column 8, line 7 - line 63 -- --------	1-5

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9706099 A1	20/02/97	AU 703767 B	01/04/99
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